

CHAPTER I

INTRODUCTION

1.1 Motivation

Production of ultrafine-particle materials is one of the most challenges of science and technology today. Several chemical methods have been investigated to prepare and control these nanosized particles (i.e., less than 100 nm.) in both industry and academia. They concern with their special characteristics and fundamentally physical and chemical phenomena relating to the formation mechanisms. Such a colloidal system is currently fascinating the scientific world. It is an important technique for many industrial applications.

Colloidal particles with a narrow-sized distribution can be prepared either by the gas-phase aerosol formation method or liquid-phase precipitation method. Each method has its own advantages. The liquid-phase precipitation method appears to be more versatile and controllable than the another. It has been achieved to synthesize many kinds of uniform particles, such as metal oxides, sulfides, nitrides, carbides, and carbonates, with a wide range from micrometer to nanometer. This method requires a particular chemical reaction in polymerization of specific precursor to form colloidal particles in liquid phase. In order to form the colloidal particles with the desired dimension and size distribution, the rate of polymerization of reactant and the stability of the outcome polymerized species have to be controlled for the entirely reaction period (Solans and Kunieda, 1995).

The formation of inorganic materials in aqueous or aqueous compatible (e.g., alcohol) media has been accomplished in uniform micrometer dimensions

(i.e., 0.1-10 μm). Stober et al. (1968) synthesized the silica particles in a short-chain alcohol solvent with controlled amounts of water and ammonia. In their work, the hydration of particle surfaces and the electrostatic repulsion (the osmotic force) were used to stabilize the inorganic particles. These forces, in general, are relatively weak. They cannot provide a sufficient repulsion to prevent the aggregation since the particles are too small when they collide. Therefore, nano-particles, with sufficient stability and uniformity, are difficult to be prepared in aqueous alcohol solution. The need of some materials with specific function and performance (i.e., catalysts with ultrahigh surface areas, photosensitive devices) triggers the interests in obtaining inorganic colloidal particles with precise dimension and small-sized distribution. Thus, W/O microemulsion system, a liquid-phase precipitation method, plays an important role in synthesizing these uniform particles.

Reverse micelle or water-in-oil microemulsion is the nano-droplets of aqueous solution dispersed in continuous oil phase, which are isolated by an interfacial film from aggregation of surface-active molecules. The head of the molecule is known as hydrophilic, liking water, while the exterior portion is known as hydrophobic, avoiding water. In each unit of micelle, water will penetrate into the center core of sphere that aggregated from surfactant molecules. Typically, their diameters are approximately 5 to 25 nm and surrounded by monolayer of surfactant molecules in the continuous hydrocarbon (i.e., heptane, isooctane, cyclohexane) media. The microemulsion is well known in terms of spontaneous formation, clear appearance, thermodynamic stability, homogenous disperse, and low viscosity (Evans, 1994). These attractive characteristics render in many industrial applications. Since this thermodynamically compartmentalization has great potential, it is used to produce the uniform particles for many applications. Microemulsion droplets do not only act as tiny-reactors for hosting the reactions but also

perform as steric stabilizers to inhibit the coagulation of precipitated resultant during the reaction period. The widespread use of and interests in microemulsions are based mainly on the large interfacial areas, high soluble capacity for both hydrophilic and hydrophobic compounds, and ultralow interfacial tensions that occur when they coexist with excess aqueous and oil phases (Solans and Kunieda, 1995).

In recent years, the preparation of ultrafine particles in microemulsions offers a novel and versatile technique. Many technological applications have been developed, such as catalysis, high-performance ceramic materials, wastewater treatment materials, microelectronic devices, and high-density magnetic recording materials. A number of materials have been successfully synthesized in nanoscale. Some examples are such metal oxide (e.g., Al_2O_3 , Fe_2O_3 , TiO_2), metal sulfide (e.g., CdS), metal carbonate (e.g., CaCO_3), and organic oxide (e.g., SiO_2). The compartmentalized droplets and thermodynamic stability of microemulsion media are able to control shape, the particle size, and; correspondingly, size distribution of these particles. This method is not only used to synthesize metals, ceramics, or composites but also used to improve magnetic, mechanic, electronic, and optical properties of materials. Nanosized silica particles are essentially utilized in the semiconductor industry (e.g., microprocessor chip), as a component of coating, inking, and painting materials, and catalyst supporter (Solans and Kunieda, 1995).

The synthesis of small size distribution of silica particles by hydrolysis and condensation of silica-alkoxide ($\text{Si}(\text{OR})_n$) in homogeneous alcoholic solution of water and ammonia catalyst has been successfully done by Stober et al. (1968). They studied the overall reaction regarding the silica particle formation from tetraethyl orthosilicate (TEOS) which is a fashioned synthesis method in the current world. Later, Boutonnet et al. (1982) performed the first synthesis of ultrafine metal particles in the range of 3-5 nm (i.e., Pt, Pd, Rh, and Ir) by

reducing metal salts in water pools of W/O microemulsion. By using this technique, monodispersed particles could be formed. Since then, several experiments have been conducted on using microemulsions to synthesize different types of nanoparticles. They also put emphasis on the physiochemical principles underlying the formation. Another group of researchers, Arriagada and Osseo-Asare (1995) studied on the silica particle formation by utilizing W/O microemulsion system for TEOS hydrolysis. They were able to control the dimension and size distribution by varying the water and surfactant concentrations in the W/O microemulsion system. Recently, Chang and Fogler (1996) have intriguingly investigated the fundamental understanding of the entire mechanism of the nucleation and kinetics of silica particle growth in W/O microemulsion system. They revealed the relationship between the rate of silica particle growth and the rate of TEOS hydrolysis and condensation. Moreover, They investigated the effects of types of surfactant, and oil, and including the influence of surfactants, water, and oil's concentrations on the growth rate and the particle size.

All of the above works can be employed to synthesize silica particles from the hydrolysis of typical precursor (TEOS) with base catalyst, aqueous ammonia. They revealed the synthesis procedure and mechanism of silica particle formation in W/O microemulsion. However, the influence of the alkyl groups of precursor in the terms of carbon number has not been studied. Previous understanding has just suggested that increasing of alkyl groups will induce the reduction in the rate of hydrolysis, since the partial charge distribution of silica atom decreases (Livage, 1982).

Although the effects of different kinds of alcohol on the interfacial properties of the microemulsion droplets have been continuously studied, final size and size distribution cannot be precisely controlled. Arriagada and Osseo-Asare (1995) studied the influence of benzyl alcohol in the AOT W/O

microemulsions. Esquena and Tadros (1997) have studied the effect of the concentration of different types of alcohol on the final particle size. They used block copolymer and nonionic surfactant (polyethylene oxide) to synthesize the monodispersed silica particles. The average size of silica particles was increased as the concentration of alcohol increased. Nevertheless, the effects of alcohol on its dimensions and the rate of precursor hydrolysis have not been attempted so far.

1.2 Objectives

As mentioned earlier, there are no attempts to investigate the effect of structural silica alkoxide precursor (i.e., hydrocarbon groups, R) on the rate of silica particle growth and to control the silica particle size distribution by using alcohol. This work was concerned upon the hydrolysis of tetrabutyl orthosilicate (TBOS) via the aqueous ammonia based catalyst in nonionic surfactant W/O microemulsion droplets to form silica particles. The main objectives were to determine the fundamental kinetics of TBOS hydrolysis and mechanisms of silica particle formation and growth in microemulsion droplets. The effect of concentration of butanol, as a co-surfactant on the rates of TBOS hydrolysis and silica particle formation was also investigated in this study.